[Second Edition.]

PATENT SPECIFICATION

Convention Date (Austria): May 21, 1926.

271,401

Application Date (in United Kingdom): Nov. 22, 1926. No. 29,471 / 26.

Complete Accepted: June 16, 1927.

COMPLETE SPECIFICATION

Improvements in and relating to Thermionic Valves and Methods of Manufacturing the same.

I, ALEXANDER JUST, an Austrian subject, of Arbeitergasse 46, Vienna, Austria, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to thermionic valves such as are used as sending and receiving valves for wireless telegraphy and the like, and more particularly to the electron-emitting cathodes for such valves and methods of making the same.

The cathodes of such valves have hitherto usually consisted either of pure tungsten or tungsten to which has been added a small quantity of thorium, or of a platinum alloy, which is either impregnated or coated with the oxide of one or more of the alkaline earth metals. These so-called oxide cathodes possess considerably greater power of electron-emission than those cathodes for example, which consist of pure tungsten.

The present invention consists in a cathode composed of a highly refractory metal or metal alloy containing or coated with certain sulphides, and in the hereinafter described methods of manufacturing such a cathode.

It has been found, that certain sulphides possess an equally great, and indeed in some cases an even greater electron-emitting capability, than the oxides hitherto suggested.

The sulphides possessing this property are the sulphides of zinc, the alkaline earth metals (calcium, strontium, barium) and the sulphides of the rare earth metals (cerium, erbium, yttrium, lanthanum, thorium, zirconium, neodymium, praseodymium and others).

The term "highly refractory metals" as used in the present specification is to be understood as metals having a melting point which exceeds 1000° C. Thus for instance copper, the melting point of which is above 1000° C. will be considered as a highly refractory metal so far as the present invention is concerned.

The two component elements, the metal and sulphide, of a cathode made according to the present invention, may be employed, either in the form of a homogeneous mixture, or the cathode may consist of a metallic core and a coating of the sulphide mentioned.

It has further been found that the sulphides are particularly effective, when they possess the property of phosphorescence, and/or when they possess the composition of phosphorescing sulphides. It is possible that the phosphorescence of such bodies may bear some relation to their capacity for electron-emission, and this may be an explanation of this phenomenon.

Virgil Klatt and Philipp Lenard have established the fact, that chemically pure sulphides are either entirely non-phosphorescent or only very slightly phosphorescent and that the phosphorescence is due to the presence of very slight traces of sulphides of the heavy metals. Pure calcium sulphide, for example, is entirely non-phosphorescent, but it becomes highly phosphorescent on the addition of a very small trace of sulphide of copper, although the calcium sulphide contains only 0.00008 to 0.0003 parts of sulphide of copper, to one part calcium sulphide.

By "phosphorescent sulphides" as used above it is to be understood that such sulphides are intended to contain an extremely small addition of the heavy metal sulphides such as the sulphides of copper, cadmium, bismuth, thallium,

[*Price* 1.-.]

uranium, tin, manganese, silver and lead.

The phonomenon of phosphorescence has been studied in connection with the sulphides of zinc, calcium, strontium and barium, but no reliable data have been obtained regarding the phosphorescence of the sulphides of the metals of the rare earths. It has however been observed, that in connection with the latter, the emissions of electrons is increased by the presence of slight traces of other sulphides.

In many cases fovourable results are obtained by employing mixtures of two or more sulphides.

The employment as the highly refractory metals of molybdenum and its alloys, also of platinum and platinum alloys has been found to be particularly advantageous.

The employment of platinum and other precious metals is of particular advantage when a sulphurizing process is employed, during the production of the cathode (i.e. heating in sulphur fumes or in a sulphuretted hydrogen atmosphere) because the precious metals are not attacked by the sulphur and will not be converted into sulphides.

In cases in which the sulphide is incorporated in the metal, the employment of the expensive precious metals may be obviated.

The manufacture of cathodes according to this invention may be effected either by producing a filament or wire from a homogeneous mixture of metal and sulphide, or by coating a metallic wire or filament with the sulphides. To produce a homogeneous metal sulphide body according to one method of carrying this invention into effect the highly refractory metal for example molybdenum is taken in a finely divided amorphous condition, as it is obtained by the reduction of molybdenum trioxide with hydrogen and is thoroughly mixed with a small quantity of one or several of the above mentioned sulphides. For example 95 to 98 parts of molybdenum are mixed with 5 to 2 parts of calcium sulphide. This mixture is worked up to a coherent body by the now well know method of first pressing the same to the form of a bar which after having been subjected to a sintering process is hammered and finally drawn to a wire. Platinum may be treated in the same manner, platinum in the black powdered form being advantageously chosen as the initial material. Instead of the ordinary sulphide, phosphorescent sulphide, produced in any well known manner may be added to the metal.

When working with precious metals, such as platinum for example, instead of adding sulphide to the amorphous metal powder, the metal in question may be added to very finely divided alkaline earth metal such as calcium powder or a rare earth metal, or a mixture of such metals or their oxides to which may be added eventually, a corresponding very small quantity of a heavy metal or heavy metal compound to produce the phosphorescence. In this case metal wires are obtained, which will have to be subjected to a sulphurising process. This may be effected by heating the metal wire in sulphur vapour or in an atmosphere of sulphuretted hydrogen, advantageously in the presence of free hydrogen. The heating may be effected by passing an electric current through the wire. In this sulphurizing process, the calcium and also the small trace of the heavy metal such as copper which have been added are converted into sulphides, whilst the precious metal is not attacked and remains as metal. Instead of the calcium metal, calcium oxide may be added, which is also converted into calcium sulphide in the sulphurizing process.

The present process renders it possible, by simple sulphurization to convert any so-called oxide-cathode into a sulphide cathode.

Instead of employing amorphous, pulverised metal, or metal in powdered form, molten metal may be employed as the initial material For example, molten platinum or a platinum-nickel-alloy in a molten state with the corresponding quantity of sulphide or phosphorescing sulphide added may be employed and the mass after having been allowed to harden, could be further worked up to form wire in any well known manner. Furthermore molten platinum could be alloyed with the corresponding quantity of calcium or zinc or with others of the metals mentioned or with a mixture of these metals, the mass then being worked up to form a wire and then finally subjected to the sulphurising process. If it is desired to employ phosphorescing sulphides and to produce these from their components in situ care must be taken that the addition of the heavy metal takes place exactly within the prescribed limits. For example, if calcium sulphide is employed, the addition of copper must not exceed 0.0003 parts of copper to one part of calcium oxide, whilst for bismuth it must not exceed 0.0012 parts to one part of calcium oxide. If manganese is employed, the contents in manganese

may be as much as .03 parts to one part of calcium oxide.

If it is required to produce metal filaments having a coating of sulphide, platinum or platinum iriduim may be coated in any known manner with calcium and the latter converted into calcium sulphide by subjecting it to a sulphurizing process, the coating in this case instead of being of pure calcium may consist of calcium containing traces of copper or bismuth. It is possible by the use of this invention to convert any of the so-called oxide-cathodes hitherto proposed having an oxide coating into a sulphide cathode by sulphurization. It is also possible to apply the sulphide to the surface of the metal wire in any well known manner and subsequently to fix the coating by glowing or heating to incandescence in a suitable inert atmosphere such as nitrogen. The sulphide cathodes produced by one or other of the methods comprising the present invention, possess the advantage compared with the oxide cathodes, that their ohmic resistance is less than that of the oxide cathodes. This is due to the fact that generally speaking, the sulphides are better conductors than corresponding oxides.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:—

1. An electron-emitting cathode for a thermionic valve consisting of a refractory metal or metal alloy containing or coated with one or more sulphides of the alkaline earth metals or zinc or rare earth metals.

2. A cathode as claimed in Claim 1 in which the sulphides possess the property of phosphorescence or have the composition of phosphorescing sulphides.

3. A cathode as claimed in Claim 1 consisting of a homogeneous mixture of metal and sulphide.

4. A cathode as claimed in Claim 1 consisting of a core of metal or metal alloy having a coating of sulphide.

5. The method of manufacturing an electron emitting cathode for thermionic valves which consists in mixing a refractory metal in a finely divided condition with a small quantity of a finely divided sulphide of a rare earth metal, forming the mixture into a coherent body, sintering the body and finally mechanically working it into wire.

6. The method of manufacturing an electron-emitting cathode for thermionic valves which consists in mixing a refractory metal in a finely divided amorphous state with a small quantity of alkaline earth metal or a rare earth metal or a mixture of such metals or their oxides, forming the mixture into wires and finally heating in a sulphurizing atmosphere to convert the alkaline earth or rare earth metals or oxides into sulphides.

7. The method of manufacturing an electron emitting cathode for thermionic valves which consists in melting a refractory metal or alloy and adding to the molten mass a small quantity of an alkaline earth metal or rare earth metal or mixture of such metals, and forming the resultant mixture into wires by any well known method, the added metals being finally converted into sulphides by heating the wire in a sulphurizing atmosphere.

8. The method of manufacturing an electron emitting cathode for a thermionic valve which consists in mixing a refractory metal in a finely divided amorphous state with small quantities of phosphorescing sulphides of zinc, calcium strontium barium or of the metals of the rare earths or mixtures of such sulphides, pressing the mixture into bars subjecting the bars to heat to sinter them and finally mechanically working the sintered bars to form wires.

9. The method of manufacturing an electron-emitting cathode for a thermionic valve which consists in mixing a refractory metal in a finely divided amorphous state with a small quantity of an alkaline earth metal or a rare earth metal or a mixture of these metals or with the oxides of these metals, adding a very small quantity of a heavy metal such as copper, working the whole into a coherent body at a high temperature, mechanically working the body into wires and finally subjecting the wire to a sulphurizing process to convert the alkaline earth, rare earth and heavy metals or oxides into sulphides.

10 In the method of manufacturing an electron-emitting cathode as claimed in Claim 7, the addition to the molten mass of a trace of a heavy metal such as copper, substantially as and for the purpose specified.

11. The method of manufacturing an electron-emitting cathode for thermionic valves which consists in subjecting a so-called oxide cathode to a sulphurizing process to convert the oxide into sulphide.

Dated this 19th day of November, 1926.

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Abingdon: Printed for His Majesty's Stationery Office, by Burgess & Son.
[Wt. 51A.—50/10/1929.]